CONTENTS

| ACKNOWLEDGEMENTS | ii |
|--|-----|
| LIST OF FIGURES AND TABLES | iii |
| ABSTRACT | vii |
| CHAPTER 1. INTRODUCTION | |
| 1.1 Inspiration for this Project | 1 |
| 1.2 Background Information | 4 |
| 1.3 Foundation Work | 9 |
| 1.4 Objectives | 13 |
| CHAPTER 2. EXPERIMENTAL | |
| 2.1 Materials and Apparati | 16 |
| 2.2 Methods | 17 |
| CHAPTER 3. SURFACE CHARACTERIZATION TECHNIQUES | |
| 3.1 Ellipsometry | 20 |
| 3.2 Contact Angle Goniometry | 25 |
| 3.3 Atomic Force Microscopy | 29 |
| 3.4 X-ray Photoelectron Spectroscopy | 32 |
| CHAPTER 4. RESULTS AND DISCUSSION | |
| 4.1 Solution-phase Silanization | 35 |
| 4.2 Vapor-phase Silanization | 51 |
| CHAPTER 5. CONCLUSIONS | 67 |
| REFERENCES CITED | 71 |

ACKNOWLEDGEMENTS

Foremost, I would like to express my sincere gratitude to my advisor, Prof. Wei Chen, for the continuous support of my study and research, for her inspiration, patience, and immense knowledge.

I would also like to thank the rest of my thesis committee, Prof. Jeffrey A. Knight and Prof. Himali D. Jayathilake, for their encouragement and insights.

I thank my fellow labmates in Wei's Group: Dr. Maria Felisa Zuniga, Emily Asenath Smith, Insun Yoon, Shelly Hsiao, Dana Jutras, Alison Erlwanger, Lanhe Zhang, and Mimi Hang. In particular, I am grateful to Dr. Zuniga for her guidance.

LIST OF FIGURES AND TABLES

| Figure 1. Covalent attachment of 3-aminopropyltriethoxysilane to a silica surface: (a) basic mechanism of silanization, (b) intra-molecular catalysis by amine, and (c) inter-molecular catalysis by amine. | 5 |
|---|----|
| Figure 2. Possible conformations of 3-aminopropyltriethoxysilane on a silica surface. | 7 |
| Figure 3. Polymerization of 3-aminopropyltriethoxysilane on a silica surface: (a) vertical and (b) horizontal. | 7 |
| Figure 4. Intra- and inter-molecular catalysis of the hydrolysis of siloxane bonds between 3-aminopropyltriethoxysilane and a silica surface. | 8 |
| Figure 5. SAMs derived with (a) tri-alkoxy aminosilane, (b) di-alkoxy aminosilane, and (c) mono-alkoxy aminosilane. | 9 |
| Figure 6. Examples of light polarization: (a) linearly, (b) circularly, and (c) elliptically polarized light. | 21 |
| Figure 7(a). Law of reflection and (b). Snell's law. | 22 |
| Figure 8. Reflections and refractions at multiple interfaces. | 23 |
| Figure 9. Ellipsometer components and operation schematic. | 24 |
| Figure 10. Static contact angle. | 26 |
| Figure 11. Measurement of dynamic contact angles: (a) an advancing angle and (b) a receding angle. | 27 |
| Figure 12. Atomic force microscope components and operation schematic. | 31 |
| Figure 13. X-ray photoelectron spectroscopy at two take-off angles: 15° and 45° . | 33 |
| Figure 14. X-ray photoelectron spectrometer components and operation schematic. | 34 |
| Figure 15. Thickness of aminosilane-derived layers before and after 24-h exposure to water. Solution-phase silanization was carried out in | 39 |

| anhydrous toluene at 70 °C for 24 h. | |
|--|----|
| Figure 16. AFM images (1 μ m×1 μ m, height scale at 20 nm) of AEAPTES-derived layers. | 41 |
| Figure 17. Thickness of APTMS- and AEAPTES-derived layers. Solution-phase silanization was carried out in anhydrous toluene at 70 °C for 24 h under different ambient humidity. | 42 |
| Figure 18. Thickness of aminosilane-derived layers against reaction time: (a) AEAPTMS and (b) AHAMTES. Solution-phase silanization was carried out in anhydrous toluene at 70 °C for 1 h, 2 h, and 24 h, respectively. | 43 |
| Figure 19. AFM images (1 μ m×1 μ m, height scale at 20 nm) of AHAMTES-derived layers. | 45 |
| Figure 20. Thickness of aminosilane-derived layers before and after 24-h exposure to water and the percent of remaining thickness. Solution-phase silanization was carried out in anhydrous toluene at 70 °C for 24 h. | 47 |
| Figure 21. Thickness of APTES- and AHAMTES-derived layers against hydrolysis time (1 h, 3 h, 12 h, and 24 h). Solution-phase silanization was carried out in anhydrous toluene at 70 °C for 24 h. | 48 |
| Figure 22. Thickness of APDMES-derived layers before and after 24-h exposure to water against reaction time. Solution-phase silanization was carried out in anhydrous toluene at 70 °C for 1 h, 2 h, and 24 h, respectively. | 49 |
| Figure 23. Thickness of aminosilane-derived layers before and after exposure to water. Vapor-phase silanization was carried out at 70 °C for 24 h. | 56 |
| Figure 24. Percent loss of thickness against hydrolysis time: (a) APTES-derived layers and (b) AEAPTES-derived layers. Vapor-phase silanization was carried out at 90 °C for 24 h or 48 h. | 60 |
| Figure 25. AFM images (1 μ m×1 μ m, height scale at 5 nm) of aminosilane-derived layers: (a) clean wafer, (b) APTES-derived layers prepared by 24-h silanization, (c) APTES-derived layers prepared by 48-h silanization, (d) AEAPTES-derived layers prepared by 24-h | 61 |

| silanization, and (e) AEAPTES-derived layers prepared by 48-h silanization. The mean roughness for each condition is ~1 Å. All the reactions were carried out under purged conditions at 90 °C. | |
|---|----|
| Figure 26. XPS of AEAPTES-derived layers: (a) initial and (b) after 24-h exposure to water. Red features are associated with take-off angle of 15° and blue features are associated with take-off angle of 45°. | 63 |
| Figure 27. Thicknesses, contact angles and atomic compositions of aminosilane-derived layers: (a) APTES and (b) AEAPTES. Vaporphase silanization was carried out at 90 °C for 48 h under purged conditions. The standard deviations in the thickness and contact angle are 1 Å and 2°, respectively. The take-off angle for XPS is 15°. | 65 |
| Figure 28. Percent loss of nitrogen content of aminosilane-derived layers based on XPS analysis at the take-off angle of 15°. | 66 |
| Figure 29. Molecular structure of triethoxysilyl undecanal. | 69 |
| Table 1. Three groups of silane coupling agents. | 15 |
| Table 2. Thickness and water contact angle (θ_A/θ_R) data of some aminosilane-derived layers before and after 24-h exposure to water. | 38 |
| Table 3. Thickness and water contact angle (θ_A/θ_R) data of some aminosilane-derived layers before and after 48-h exposure to water. | 40 |
| Table 4. Thickness of APTES- and AHAMTES-derived layers before and after exposure to water. | 47 |
| Table 5. Thickness and water contact angle (θ_A/θ_R) data of APDMES- derived layers before and after 24-h exposure to water. | 49 |
| Table 6. Thickness of AEAPTES- and AEAPTMS-derived layers before and after 48-h exposure to water. | 54 |
| Table 7. Thickness of the Group I and II aminosilane-derived layers before and after exposure to water. | 55 |
| Table 8. Thickness of AHAMTES-derived layers before and after 48-hexposure to water. | 57 |
| Table 9. Thickness and contact angle (θ_A/θ_R) data of aminosilane- derived layers before and after exposure to water: (a) APTES and (b) | 59 |

AEAPTES.

| 64 |
|----|
| |
| |
| 70 |
| |
| |

ABSTRACT

Aminosilanes are commonly used to functionalize silica substrates. The hydrolytic stability of aminosilane-derived layers is a major consideration in choosing suitable reagents for aqueous applications. We recently reported that aminosilane-derived layers prepared with the most widely used silane coupling agents, 3-aminopropylalkoxysilanes, suffer extensive loss upon exposure to water at moderate temperatures. This is likely caused by siloxane bond hydrolysis catalyzed by the amine functionality via the formation of a stable five-membered intermediate. In this study, we evaluated the performances of five silane coupling agents, 3-aminopropyltriethoxysilane (APTES), 3-aminopropyltrimethoxysilane (APTMS), N-(6-aminohexyl)aminomethyltriethoxysilane (AHAMTES), N-(2aminoethyl)-3-aminopropyltriethoxysilane (AEAPTES), and N-(2-aminoethyl)-3aminopropyltrimethoxysilane (AEAPTMS). They have the general structures of $NH_2(CH_2)_kSi(OR)_3$ and $NH_2(CH_2)_nNH(CH_2)_mSi(OR)_3$, where R represents either a methyl or an ethyl group. Silanization was carried out on silicon wafers in anhydrous toluene or in the vapor phase. The hydrolytic stability of aminosilanederived layers was correlated with the reaction conditions and the silane structural features.